

EXPERIMENTAL INVESTIGATION OF POTENTIAL HCL AND HF MINERAL BUFFERS ON VENUS

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Introduction

- ❖ The abundance of HCl in Venus' atmosphere is 0.4 ± 0.03 ppmv and HF is 5 ± 3 ppbv
- ❖ Measurements of HCl and HF in the atmosphere of Venus taken over 20 years apart reveal similar abundances suggesting that both gases are in equilibrium [2]
 - ❖ This alludes to a yet to be determined chlorine and fluorine buffer system with the surface
- ❖ Several researchers have used thermodynamic modeling to investigate the interactions between these gases and potential minerals on the surface of Venus [1, 3-7]
 - ❖ However, thermodynamic calculations use experimental data to model reactions, and very little experiments have been completed at Venus relevant conditions

Objectives:

1. Investigate any interactions that may occur between a single mineral with either HCl or HF to produce a chlorine- or fluorine-bearing mineral
2. Investigate if the hydroxyl group in some hydrated silicates can interact with HF and be replaced with fluorine
3. Investigate if mineral mixtures can be sinks for Cl-minerals or F-minerals

Methods

Samples:

- ❖ Total: 27
- ❖ Mineral chips were cut and polished using SiC, diamond paste, and colloidal silica to a 50 nm polish
- ❖ Powders were ground using a mortar & pestle and sieved to 100 μ m

Glenn Extreme Environment Rig (GEER) [8-9]:

- ❖ Temperature and Pressure: 460°C and ~93 bar
- ❖ Gas: CO₂, N₂, SO₂, H₂O, CO, COS, H₂S, HCl, and HF
- ❖ Length of Time: 60 days
- ❖ Gas Chromatograph (GC)

Instruments for Analysis:

- ❖ X-Ray Diffraction (XRD)
- ❖ Scanning Electron Microscope (SEM)
- ❖ Energy-Dispersive x-ray Spectroscopy (EDS)
- ❖ X-ray Photoelectron Spectroscopy (XPS)
- ❖ Brunauer, Emmett and Teller (BET) surface area analysis

Objective 1	Objective 2	Objective 3
Nepheline NaAlSiO ₄	Ferrohornblende Ca ₂ (Fe ²⁺ ₄ Al)(Si ₇ Al)O ₂₂ (OH) ₂	Wollastonite + Sodalite CaSiO ₃ + Na ₄ [AlSiO ₄] ₃ Cl
Albite NaAlSi ₃ O ₈	Tremolite Ca ₂ Mg ₅ Si ₈ O ₂₂ (OH) ₂	Microcline + Enstatite KAlSi ₃ O ₈ + MgSiO ₃
Enstatite MgSiO ₃	Phlogopite KMg ₃ AlSi ₃ O ₁₀ (OH) ₂	Microcline + Forsterite KAlSi ₃ O ₈ + Mg ₂ SiO ₄
Wollastonite CaSiO ₃	Pargasite NaCa ₂ Mg ₄ Al ₃ Si ₆ O ₂₂ (OH) ₂	Nepheline + Diopside + Enstatite NaAlSiO ₄ + CaMgSi ₂ O ₆ + MgSiO ₄
Forsterite Mg ₂ SiO ₄	Muscovite KAl ₃ Si ₃ O ₁₀ (OH) ₂	Quartz + Diopside + Enstatite SiO ₂ + CaMgSi ₂ O ₆ + MgSiO ₃
	Brucite Mg(OH) ₂	

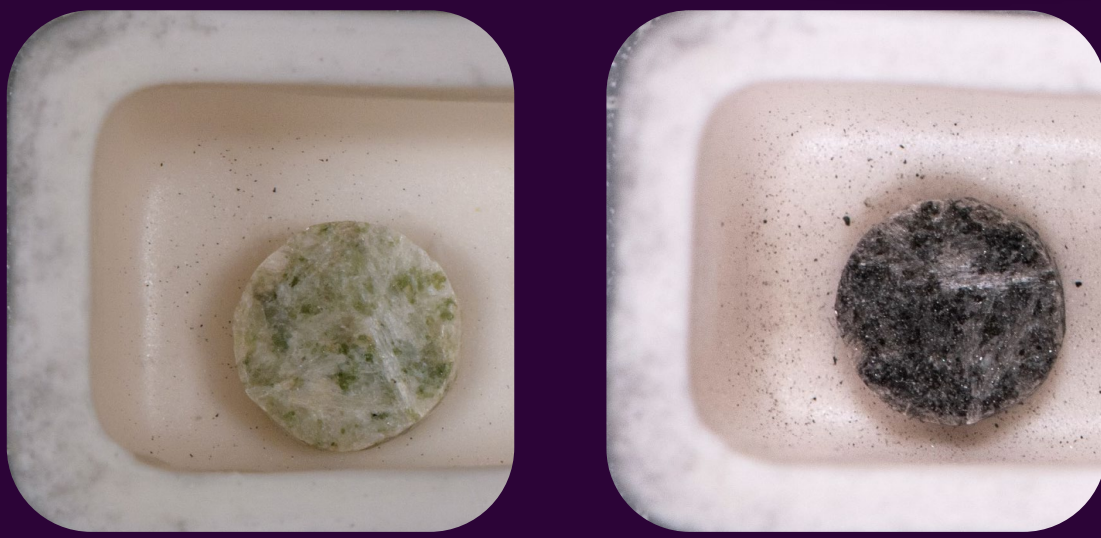
Table 1: All samples that were selected to address Objectives 1, 2, and 3 in this project

CO ₂	N ₂	SO ₂	CO	COS	H ₂ S	H ₂ O	HCl	HF
96.5 ± 0.8%	3.5 ± 0.8 %	150 ± 30 ppmv	17 ± 1.4 ppmv	4.4 ± 1 ppmv	3 ± 2 ppmv	30 ppmv	0.4 ppmv	5 ppbv

Table 2: Starting gas composition in the 60-day GEER test



Figure 1: Wollastonite before (left) and after (right) the experiment



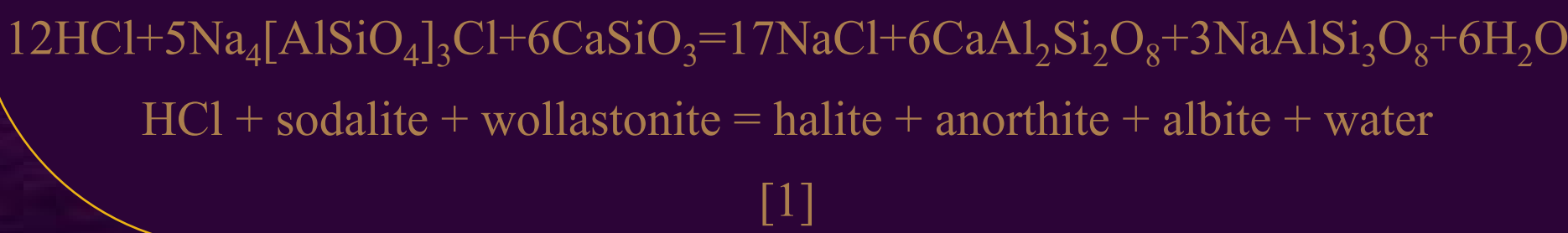
A	XPS	S (at %)	F (at %)	Cl (at %)
	Wollastonite Chip	nd	nd	nd
	sputtered 1 min (100 Å)	nd	nd	nd
	Wollastonite Chip 60 Days in GEER	2.9 ^{SO4}	0.1	nd
	sputtered 1 min (100 Å)	1.9 ^{SO4}	0.1	nd

B	XPS	S (at %)	F (at %)	Cl (at %)
	Wollastonite Powder	nd	nd	nd
	sputtered 1 min (100 Å)	nd	nd	nd
	Wollastonite Powder 60 Days in GEER	3.1 ^{SO4}	0.1	nd
	sputtered 1 min (100 Å)	2.2 ^{SO4}	nd	nd
	sputtered 2 min (200 Å)	1.9 ^{SO4}	nd	nd

Table 3: Wollastonite was selected as one of the minerals to address Objective 1. The above tables show XPS data before (A) and after (B) the experiment. S is present as a sulfate on both the chip and powder after the experiment. Cl is not present on any sample. Some F is present at depth in the chip, but not in the powder

XPS	S (at %)	F (at %)	Cl (at%)
Sodalite + Wollastonite Powder	nd	nd	1.5
sputtered 1 min (100 Å)	nd	nd	1.7
Sodalite + Wollastonite Powder 60 days in GEER	1.9 ^{SO4}	nd	1.1
sputtered 1 min (100 Å)	1.1 ^{SO4}	nd	1.3

Table 4: The sodalite + wollastonite mixture was selected as one of the mixtures to address Objective 3 and has been theorized to react via the equation below. The above table shows XPS data before and after the experiment. S is present as a sulfate after the experiment. F is not detected in the sample. The Cl abundance after the test is similar to the abundance before the test



Conclusions

- ❖ The vast majority of the samples exhibited a color change into a dull white/grey after the experiment
- ❖ At this time, it cannot be determined if any of the fluorine or chlorine are merely adhered to the surface of the samples, or interacted with the samples to produce secondary minerals
- ❖ Sulfur is present on all samples, but the oxidation state varies depending on the cations present in the sample
- ❖ Further analysis using SEM/EDS, microprobe and nanoSIMs are planned in the future

Results

We are unable to display all of the data due to the number of samples investigated in this project. We have chosen a few samples that address each of the objectives to present on this poster. All data is preliminary and further analysis is currently underway



Figure 2: Tremolite before (left) and after (right) the experiment

XPS	Surface Area (m ² /g)
Tremolite Powder	5.0888 m ² /g
Tremolite Powder 60 days in GEER	5.5730 m ² /g

Table 5: The surface area of tremolite before and after the experiment was determined using BET surface analysis. The sample's surface area increased marginally by the end of the experiment

A	XPS	S (at %)	F (at %)	Cl (at %)
	Tremolite Chip	nd	0.3	nd
	sputtered 1 min (100 Å)	nd	0.3	nd
	Tremolite Chip 60 days in GEER	0.8 ^{SO4}	0.8	0.1
	sputtered 1 min (100 Å)	<.1 ^{SO4}	0.6	<.1

B	XPS	S (at %)	F (at %)	Cl (at %)
	Tremolite powder	nd	0.2	nd
	sputtered 1 min (100 Å)	nd	0.2	nd
	Tremolite powder 60 days in GEER	1 ^{SO4} -	1	nd
	sputtered 1 min (100 Å)	0.3 ^{S-}	0.7	nd

Table 6: Tremolite was selected as one of the minerals to address Objective 2. The tables to the left show XPS data before (A) and after (B) the experiment. S is present as a sulfate in the chip and as a sulfate and sulfide in the powder after the experiment. However, sputtering of the powder revealed that only sulfide is present at depth. The F abundance may have marginally increased as a result of the experiment. A small amount of Cl is present on the surface of the tremolite chip after the experiment

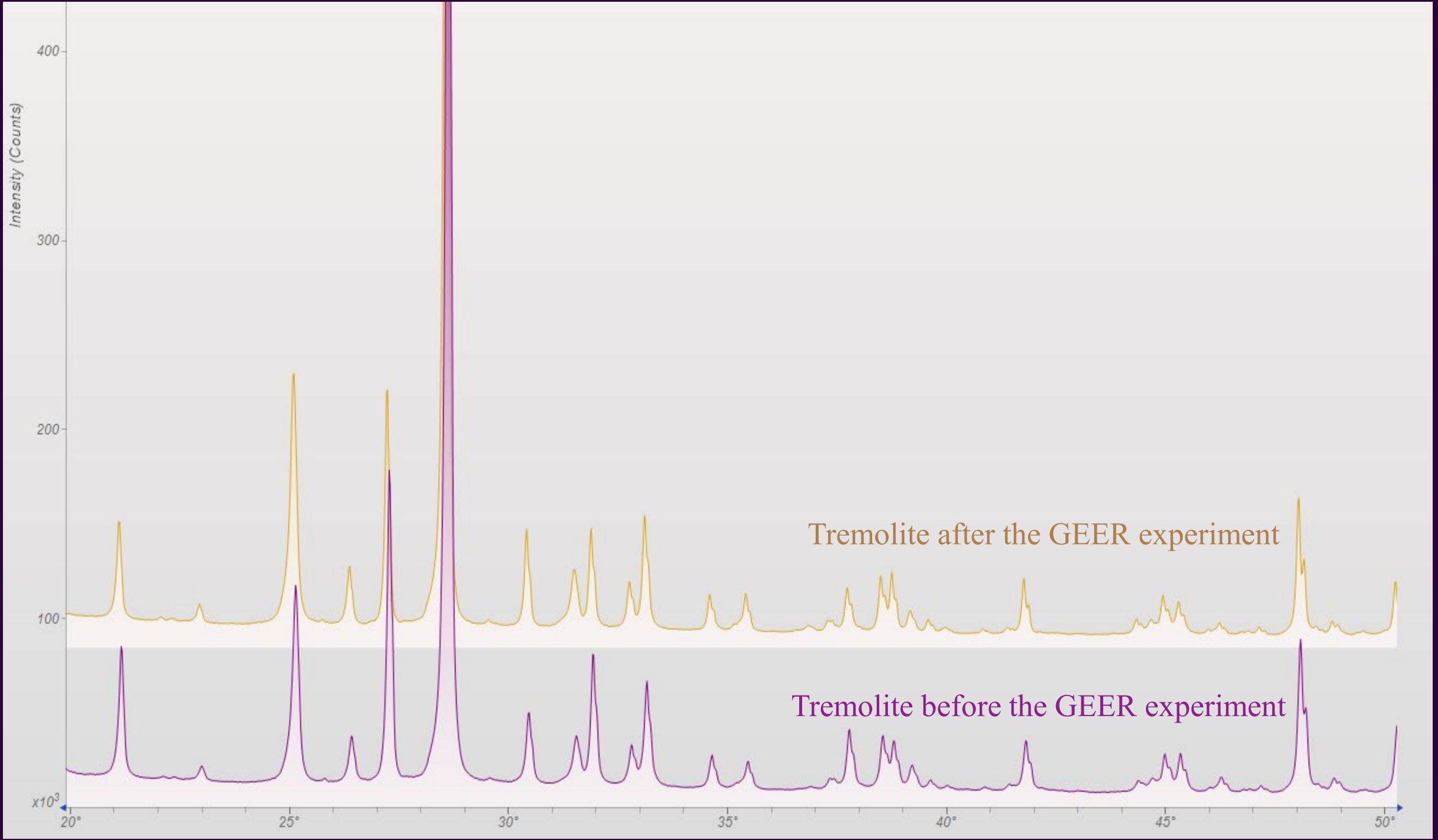


Figure 3: Zoomed in XRD spectra of tremolite before and after the GEER test. No differences were observed between the two spectra. If any changes did occur as a result of the experiment, it was not significant enough to be detected by XRD

References

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